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Rheology of Confined Polymer Melts under Shear Flow: Strong Adsorption Limit

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ABSTRACT: The dynamics of a confined polymer melt between strong adsorbing surfaces is considered theoretically. In particular the influence of bridging on the rheological behavior is investigated. It is shown that the bridges are very important for small enough shear velocities. Several regimes of qualitatively different rheological behavior depending on the shear velocity are predicted, one of the intermediate regimes being characterized by a power law decrease of the shear stress as a function of the velocity.

1. Introduction

The behavior of polymeric liquids under confinement differs in an essential way from that in the bulk if the polymer film thickness is of the order of the size of the polymer coil or smaller. This is due to the interaction between the polymer and the surface. Depending on the polymer–surface interaction, polymer chains can adsorb to the surface or be repelled by it. In the case of attractive surfaces in contact with a polymer melt an absorbed layer having a thickness of the order of the size of the polymer coil is formed. If the polymer system is confined between two plane surfaces separated by a distance smaller or comparable to the size of the polymer coil, nearly all chains are in contact with the surfaces. In this case the dynamical properties of the film strongly depend on the polymer–surface interaction and are directly connected to the dynamics characterizing the adsorbed chains.

Recent experiments[1–3] as well as molecular dynamics computer simulations,[4,5] devoted to the study of the dynamics of confined polymer films under shear flow, demonstrate that for an increasing shear velocity the behavior of the system becomes nonlinear. In addition, experiments show that under oscillatory shear with a small amplitude the behavior of the confined layer is viscoelastic, whereas for greater amplitudes a transition to liquid-like behavior occurs.

The aim of the present study is to investigate theoretically the rheological behavior of a thin polymer film confined between two plane surfaces and under shear with a constant imposed velocity, and in particular to determine the dependence of the shear stress on the imposed velocity. We distinguish three situations: a linear regime at low shear rates, an intermediate situation, when nonlinear dynamics of bridges is important, and a high shear rate regime where bridges are no longer present.

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2. Equilibrium Properties

The equilibrium properties of an adsorbed polymer layer under different conditions have been investigated in a number of previous studies.[6,7] In contrast to the case of a polymer solution near a solid surface, equilibrium properties of an incompressible melt do not depend on the interaction with the surface. Thus, in particular, polymer chains in a melted polymer layer locally obey Gaussian statistics[8,9] (which is generally known to be valid for polymers in melts—the so-called Flory theorem; see ref 8). The global effect of the solid walls on the chain statistic can be accounted for by the mirror-image principle.[10] In the equilibrium there is no long range interaction between the surfaces.[9,11]

We assume that the chains consist of N statistical segments of length a and volume per segment ϑ. The thickness of the confined film (h) is assumed to be smaller or equal to the size of the coils ($h \leq aN^{1/2}$). Hence, the area of contact per segment is ϑ/a, and an adsorbed chain has on average Na/h number of contacts with the surfaces.

It is convenient to consider a polymer chain as a sequence of blobs of size h, each blob consisting of $g_0 \sim h^2/a^2$ segments. A finite fraction of the blobs (e.g. $\sim 1/2$) must form bridges between the surfaces (a blob is called a "bridge" if it has contacts with both walls[12]); each bridge implies of order $g_0^{1/2} \sim h/a$ contacts with the surfaces. The average number of bridges per unit area is $\nu(g_0) \sim h/\vartheta g_0 \sim a^2/(h\vartheta)$.

3. Shear Stress: The Effect of Bridges

3.1. Linear Regime. Shear flow is imposed by moving one of the surfaces with respect to the other with a constant velocity u. In this case, the behavior of the polymer segments in the vicinity of the surfaces and far away from it is different. The mobility of the segments in the middle part of the confined film is determined by a friction coefficient ζ_0, whereas the motion of the adsorbed chain segments is governed by a friction coefficient ζ_1 different from ζ_0, due to the surface potential with a typical scale $\sim a$. If the polymer–surface interaction is attractive, ζ_1 might be much bigger than the friction coefficient ζ_0, $\zeta_1/\zeta_0 \gg 1$. Here it is assumed that this condition is satisfied. It is also assumed that entanglements are not important; i.e. the

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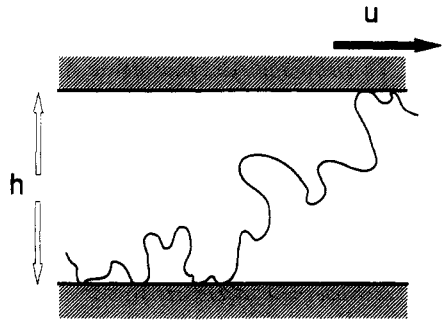

Figure 1. Bridge in the linear regime.

chain lengths considered are below the entanglement threshold.

Obviously, bridges can have an essential influence on the dynamical behavior of confined systems. In the steady state there is an equilibrium between the breakage and formation of bridges. The dynamics of formation of contacts with the surface, in the case of strong adsorption, is determined by the surface friction. Let us consider an arbitrary blob containing g segments near one of the surfaces; the blob must have $\sim g^{1/2}$ contacts with the surface. The total friction coefficient for the blob is thus given by

$$\zeta_{tot} \cong \zeta_0(g - g^{1/2}) + \zeta_1 g^{1/2} \tag{1}$$

The relaxation time (adsorption and desorption time), τ_g, is the diffusion time of the blob over a distance of its size $r_g \sim ag^{1/2}$; the effective diffusion constant is $D_g = 1/\zeta_{tot}$ (here and below k_BT is chosen as the unit of energy). Therefore

$$\tau_g \sim r_g^2/D_g = a^2 g \zeta_{tot} \cong \tau_0 g^2 + \tau_1 g^{3/2} \tag{2}$$

where $\tau_0 \sim \zeta_0 a^2$ is the relaxation time of a segment in the bulk and $\tau_1 \sim \zeta_1 a^2$ is the relaxation time near the surface. Here we will consider exclusively the case of strong adsorption: $g_0 \ll (\tau_1/\tau_0)^2$; thus the second term in eq 2 dominates and the first one can be omitted for any blob adsorbed to the surface.

When a velocity u is imposed, the bridges start to elongate, the maximum elongation force being equal to the friction force on the surface (Figure 1). If the velocity is small and the chain is Gaussian (regime 1), the friction force per one bridge is given by

$$f_t \sim u\zeta_1 g_0^{1/2} \tag{3}$$

The shear stress can be defined as the product of the friction force and the surface concentration of the bridges $\nu(g_0) \sim a^2/(h\vartheta)$

$$\sigma_t \sim (au\zeta_1)/\vartheta \tag{4}$$

3.2. Nonlinear Regime. 3.2.a. Statistics of Bridges. The response of the bridges becomes more complicated if we take into account the limited extensibility of chains.[13,14] Let us assume that a bridge consisting of g_0 segments is characterized by the following general relation between the elastic force **f** and the end-to-end distance (elongation) **r**:

$$\mathbf{f} = \frac{\mathbf{r}}{a^2 g_0}\varphi\left(\frac{\mathbf{r}^2}{a^2 g_0^2}\right) \tag{5}$$

with

$$\varphi(x) = 1 + \kappa_1 x + \kappa_2 x^2 + \ldots \quad x < 1$$

$$\varphi(1) = \infty \tag{6}$$

where $\kappa_1, \kappa_2, \ldots$ are numerical coefficients. The relation like this is valid for the freely jointed model of a chain consisting of connected rigid segments with $\kappa_1 \sim (l/a)^2$, where l is the length of the rigid segment and a is the statistical length.[15]

When the bridge is stretched, the tangential deformation r_t due to nonlinearity (5) induces an additional normal force $\Delta f_n = f_n(r_n,r_t) - f_n(r_n,r_t = 0)$ (in our case $r_n = h$). If the elongation is small, $r_t \ll ag_0$, the relation connecting the tangential and normal force can be calculated by the perturbation theory:

$$\Delta f_n \sim \frac{a^2}{h} f_t^2 \qquad f_t < \frac{1}{a} \tag{7a}$$

and the normal force is small compared to the thermal force $f_n \sim 1/h$. If $r_t \sim ag_0$ and $\varphi \gg 1$, then $f_n/f_t = \tan\alpha = h/ag_0$, where α is the angle between the slope of bridge and plane (Figure 2):

$$\Delta f_n \sim \frac{a}{h} f_t \qquad f_t > \frac{1}{a} \tag{7b}$$

The dynamics of adsorption of a blob onto the surface is governed by this additional normal force, Δf_n. If the typical energy associated with the normal force is small in comparison with k_BT; i.e. $\Delta f_n h \ll 1$, then the effect of the force is negligible. On the other hand, in the case $h\Delta f_n > 1$, the normal force strongly pulls the blob away from the surface thus preventing an adsorption of the g_0 blob. However a smaller blob with a number of segments $g < g_0$ can possibly still adsorb, since the normal force limiting the adsorption depends on g.

The condition $h\Delta f_n \sim 1$, together with eqs 3 and 7a, gives the critical velocity

$$u_1 = \frac{a}{\tau_1}\frac{a}{h} \tag{8}$$

For $u < u_1$ eq 4 is applicable. This linear regime will be denoted as regime 1.

For higher velocities, $u > u_1$, the maximum g_0 blob can no longer be adsorbed, and the typical size of a blob that can be adsorbed is $g < g_0$. A bridge in this regime consists of at least two g blobs in contact with the opposite surfaces, and a middle part containing $\sim g_0$ links.

Let us estimate g. Note that for $u > u_1$ the (maximum) friction force, $f_t > 1/a$, and therefore a bridge will be almost completely extended by the force. Immediately after formation, a bridge starts to elongate with velocity u. After a time

$$t \sim ag_0/u \tag{9}$$

it attains the maximum elongation $\sim ag_0$. At this moment the tangential stretching force reaches a maximum equal to

$$f_t \sim u\zeta_1 g^{1/2} \tag{10}$$

where g is the number of segments in the characteristic blob that manages to create surface contacts during this

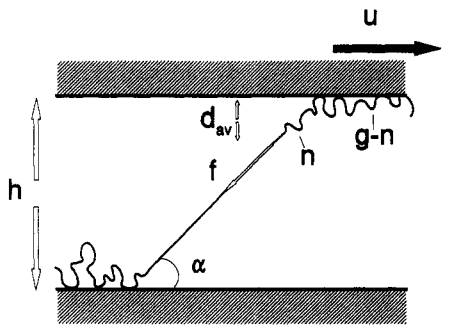

Figure 2. Bridge in the regime of strong elongation.

time t. Equating the relaxation time of a g blob (eq 2) and the elongation time, t, we get

$$g \sim (t/\tau_1)^{2/3} \sim (h^2/au\tau_1)^{2/3} \tag{11}$$

Note that $g \sim g_0$ for $u = u_1$.

Our next task is to derive an expression for the surface concentration of bridges. Let us therefore consider a polymer chain as a sequence of g blobs. Any part of the chain that has contacts with one of the surfaces must be repelled (pulled away) from the other one via the mechanism of bridge elongation. This repulsion can be formally taken into account by the condition that the concentration of the g blobs belonging to a chain in contact with one wall must tend to zero in the vicinity of the other wall. We will assume that the effect of the flow on the bridge distribution reveals itself only in this change of the boundary conditions, the distribution being quasi-equilibrium otherwise. The concentration of the g blobs at a distance x from the adsorbing surface is $\psi^2(x)$, where $\psi(x)$ is the order parameter.[8,16] Here we must introduce two parameters ψ_1 and ψ_2 that describe the distribution of blobs of the chains adsorbing to the two different surfaces. The free energy per unit area depends on ψ_1 and ψ_2 through the relation[16]

$$F \sim a^2 g \int_0^h \left[\left(\frac{d\psi_1(x)}{dx}\right)^2 + \left(\frac{d\psi_2(x)}{dx}\right)^2\right] dx \tag{12}$$

This free energy should be minimized for the appropriate boundary conditions and the condition of dense packing:

$$\psi_1^2 = 0 \qquad \psi_2^2 = 1/(g\vartheta) \qquad x = 0$$

$$\psi_1^2 = 1/(g\vartheta) \qquad \psi_2^2 = 0 \qquad x = h$$

$$\psi_1^2 + \psi_2^2 = 1/(g\vartheta) \tag{13}$$

After minimization we get

$$\psi_1^2(x) = 1/(g\vartheta)\sin^2(\pi x/2h)$$

$$\psi_2^2 = 1/(g\vartheta)\cos^2(\pi x/2h) \tag{14}$$

The surface concentration of g blobs is defined as the number of blobs per unit area inside the adsorbed layer of thickness $\xi = ag^{1/2}$ and is given by

$$\nu(g) \sim \xi\psi_1^2(\xi) \sim \frac{a}{\vartheta}\frac{a^2 g^{1/2}}{h^2} \tag{15}$$

Each bridge corresponds to one surface blob, so the concentration of the bridges is also defined by eq 15. The concentration of bridges is thus much smaller than the concentration of g_0 blobs, $\nu(g_0) \sim a^2/hv$. Therefore only one g_0 blob per

$$q \sim \nu(g_0)/\nu(g) \sim (hu\tau_1/a^2)^{1/3} \tag{16}$$

g_0 blobs form a bridge.

Now we can estimate the average "lifetime" of a g_0 blob in a free state (without bridging) as the time of order

$$t^* \sim tq \sim \tau_1(a/u\tau_1)^{2/3}(h/a)^{7/3} \tag{17}$$

This time exceeds the Rouse relaxation time of the bridge $\tau_0 g_0^2$ if the velocity $u < u^*$, where

$$u^* = \frac{a}{\tau_0}\left(\frac{a}{h}\right)^{5/2}\left(\frac{\tau_1}{\tau_0}\right)^{1/2} \tag{18}$$

As long as $u < u^*$, the quasi-equilibrium approach used to calculate the surface concentration of bridges is valid.

3.2.b. Regime 2. Let us assume that this condition is satisfied (a verification is given in the last section) and calculate the shear stress. After the time t given by eq 9 the elongation of the bridge attains its maximum value. Then the tangential force will be of the order of the surface friction force (10). In accordance with eq 7b the normal force induced by this tangential force is

$$f_n \sim \frac{1}{a}\left(\frac{u\tau_1}{a}\right)^{2/3}\left(\frac{a}{h}\right)^{1/3} \tag{19}$$

Let us consider the region $u_1 < u < u_2$ (regime 2), where the upper limit

$$u_2 = \frac{a}{\tau_1}\left(\frac{h}{a}\right)^{1/2} \tag{20}$$

is derived below. Here the normal force is in the range $1/h < f_n < 1/a$. In order to calculate the shear stress for this case we must know the average "debridging time", that is the time during which the strong friction force f_t is acting. This time can be defined as the time that is needed to move the adsorbed blob on a large enough distance d from the wall. This distance can be estimated in the following way. The chain conformation at some intermediate state of debridging is shown schematically in Figure 2: here n segments have been already pulled from the (upper) surface by the strong elastic force $f \sim f_t \sim \zeta_1 u g^{1/2} \gg 1/a$. The detached part of n segments is thus strongly stretched: its length is of order na. Therefore the typical separation of this part from the wall is

$$d_{av} \sim na \tan\alpha \sim na^2/h \tag{21}$$

This separation is irreversible (i.e. the n part cannot form contacts with the wall again) if d_{av} is larger than the typical scale of fluctuation displacement in the normal direction, d_{fl}, for the links of an n part. The latter is determined by the elastic force (which is equal to the friction force)

$$d_{fl} \sim (an/f_t)^{1/2} \tag{22}$$

The condition $d_{av} \sim d_{fl}$ gives the critical separation d, and simultaneously the critical size of the separated part. Using eqs 21 and 22, we thus get (for $n \sim g$)

$$d \sim d_{av} \sim d_{fl} \sim a(a/u\tau_1)^{2/3}(h/a)^{1/3} \quad (23)$$

Under the influence of the normal force the adsorbed blob moves out of the surface with the velocity

$$v = ua/h \quad (24)$$

Thus the "breaking time" is $\tau \sim d/v$. The average shear stress can be estimated as

$$\sigma_t \sim f_t \nu(g)\tau/t \sim \frac{1}{\vartheta}\left(\frac{a}{u\tau_1}\right)^{1/3}\left(\frac{a}{h}\right)^{4/3} \quad (25)$$

Equation 23 is valid if $d > a$. Using eq 23 the last condition can be rewritten as $u < u_2$ with u_2 given by eq 20.

3.2.c. Regimes 3 and 4. Let us consider the region of even larger velocities $u_2 < u < u_3$ (regime 3), where

$$u_3 = \frac{a}{\tau_1}\left(\frac{h}{a}\right)^2 \quad (26)$$

is defined from the condition $g \sim 1$. In this region the characteristic debridging distance $d \sim a$ and the "breaking time" is $\tau \sim a/v$. The shear stress in this case can be calculated by using eq 25

$$\sigma_t \sim \frac{1}{\vartheta}\left(\frac{u\tau_1}{a}\right)^{1/3}\left(\frac{a}{h}\right)^{5/3} \quad (27)$$

When the imposed velocity $u > u_3$ (regime 4), only one segment can attain the surface. During the time t the segment can penetrate over a distance

$$\Delta \sim a(t/\tau_1)^{1/2} \quad (28)$$

into the viscous surface layer, with $\Delta < a$. The corresponding "break time" is $\tau \sim \Delta/v$, and the shear stress is given by

$$\sigma_t \sim u\zeta_1 \nu(1)\tau/t \sim \frac{1}{\vartheta}\left(\frac{u\tau_1}{a}\right)^{1/2}\left(\frac{a}{h}\right)^2 \quad (29)$$

So far we consider the contribution of the bridges to the shear stress. The second part of the shear stress is connected with the dissipation in the bulk. This part is equal to the friction between two penetrating layers of thickness h. The calculations show that "bulk" contribution to the shear stress is

$$\sigma_t^{(b)} \sim uh\tau_0/a^2\vartheta \quad (30)$$

Equation 30 is valid if $u < u_4$, where the velocity u_4 is defined below. Note that in all the regimes considered so far the "bulk" contribution is negligible: $\sigma_t^{(b)} \ll \sigma_t$.

4. Regime of High Shear Velocities

At this point it is important to take into account the influence of the flow on the conformations of the chains. The characteristic friction force, that impacts on a bridge (on a chain part containing g_0 links), is

$$f_t \sim \zeta_0 u g_0 \quad (31)$$

This force induces an additional normal force in accordance with eq 7

$$\Delta f_n \sim \frac{a^2}{h} f_t^2 \sim \frac{a^2}{h}(u\zeta_0 g_0)^2 \quad (32)$$

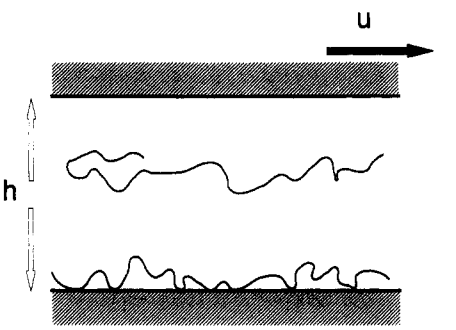

Figure 3. Chain elongation due to the flow.

Obviously, this force is smaller than the thermal fluctuation force $1/h$, if $u < u_4$, where

$$u_4 \sim \frac{a}{\tau_0}\left(\frac{a}{h}\right)^2 \quad (33)$$

Now let us assume that $u > u_4$ (regime 5). Here a bridge formation is nearly impossible: any loop (attached to, e.g., the bottom surface; see Figure 3) that might tend to form a bridge is compressed by the normal force Δf_n, eq 32, which effectively confines the loop in a layer of thickness $\xi \sim 1/\Delta f_n$ near the bottom wall. Therefore the bridge contribution to the stress is negligible in this region. In order to calculate the stress due to the chain parts that do not form bridges let us consider the blob consisting of g segments and having the typical size in the normal direction $\xi \sim ag^{1/2}$. The flow will stretch this blob by the friction force

$$f_t \sim \zeta_0 g\dot{\gamma}\xi \quad (34)$$

where $\dot{\gamma} = u/h$ is the shear rate. Let us assume that the force is large enough ($f_t > 1/a$), so that the blob is almost completely extended along the flow (its size in this direction is thus $\sim ga$). The force f_t induces the force in the normal direction, that tends to compress the blob[14]

$$\Delta f_n \sim f_t \tan\alpha \cong f_t\xi/(ga) \quad (35)$$

In the steady state this force is compensated by the thermal restoring force which is of order $\sim 1/\xi$. The condition $\Delta f_n \sim 1/\xi$ thus gives the characteristic size of the blob

$$\xi \sim a(\dot{\gamma}\tau_0)^{-1/3} \quad (36)$$

Obviously, $\xi < h$ when the shear velocity $u > u_4$. In this case the flow strongly elongates the chains, so that each chain is effectively confined in a layer of thickness ξ (Figure 3). The dissipation per unit volume is

$$D \sim \zeta_0(\dot{\gamma}\xi)^2/\vartheta \quad (37)$$

Thus the stress is

$$\sigma_t \sim \zeta_0\dot{\gamma}\xi^2/\vartheta \sim \frac{1}{\vartheta}\left(\frac{u\tau_1}{h}\right)^{1/3} \quad (38)$$

5. Discussion and Conclusions

For all regimes (1)–(5) to be realized (the full picture of the regimes is shown in Figure 4), the inequalities $u_3 < u_4$ and $u_4 < u^*$ must be satisfied. The last condition is valid, when $(h/a) < (\tau_1/\tau_0)$; that is, it coincides with the condition of validity of the whole scheme (strong friction). The first condition is valid if

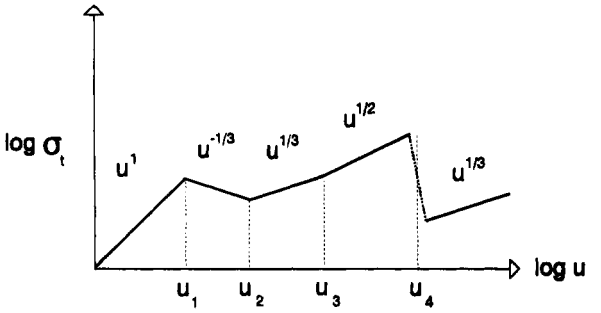

Figure 4. Plot of the shear stress vs the velocity.

$(h/a) < (\tau_1/\tau_0)^{1/4}$. Thus for the very strong friction we have the following dependence of the shear stress on the imposed velocity

$$\sigma_t \sim (u\zeta_1) \qquad u < \frac{a}{\tau_1}\frac{a}{h} \tag{39.1}$$

$$\sigma_t \sim (u\zeta_1)^{-1/3} \qquad \frac{a}{\tau_1}\frac{a}{h} < u < \frac{a}{\tau_1}\left(\frac{h}{a}\right)^{1/2} \tag{39.2}$$

$$\sigma_t \sim (u\zeta_1)^{1/3} \qquad \frac{a}{\tau_1}\left(\frac{h}{a}\right)^{1/2} < u < \frac{a}{\tau_1}\left(\frac{h}{a}\right)^{2} \tag{39.3}$$

$$\sigma_t \sim (u\zeta_1)^{1/2} \qquad \frac{a}{\tau_1}\left(\frac{h}{a}\right)^{2} < u < \frac{a}{\tau_0}\left(\frac{a}{h}\right)^{2} \tag{39.4}$$

$$\sigma_t \sim (u\zeta_0)^{1/3} \qquad \frac{a}{\tau_0}\left(\frac{a}{h}\right)^{2} < u \tag{39.5}$$

Equation 39.1 describes the linear regime, where the surface friction force is smaller than $1/a$; regime (39.2) corresponds to higher velocities implying that the maximum blob g_0 does not typically have enough time to create of the order of $g_0^{1/2}$ contacts with both surfaces. The normal force, which pulls the blob out of the surface obeys the inequality $1/h < f_n < 1/a$. The shear stress in this case decreases with increasing velocity as power $-1/3$. If a permanent velocity is imposed, the shear stress is uniquely defined by it and there is no reason for an instability. In regime (39.3), the normal force exceeds $1/a$, but the bridge has more than one contact with the surface. The shear stress increases in this case with a power (1/3). In regime (39.4) only on the order of one segment can penetrate into the viscous layer. For the very high velocities (regime 5) the flow compresses the chains, so that bridges can no longer be formed. So the bridge contribution to the stress drops rapidly in the crossover region (between regimes 4 and 5) thus giving rise to a sharp decrease of the total stress in this region. The shear stress is described by eq 39.5 in regime 5. Note this implies that viscosity $\eta = \sigma_t/\dot{\gamma} \sim \dot{\gamma}^{-2/3}$.

If the ratio (h/a) obeys the condition $(\tau_1/\tau_0)^{1/4} < (h/a) < (\tau_1/\tau_0)^{2/5}$, regimes (1), (2), (3), and (5) are all realized; if $(\tau_1/\tau_0)^{2/5} < (h/a) < (\tau_1/\tau_0)$, only regimes (1), (2), and (5) can be realized. When $(\tau_1/\tau_0) < (h/a)$, the surface friction is small and the surface slip starts to be important.[14]

Our calculations can be compared with experimental results from ref 1. The experimental plots for two types of the polymers (linear Fomblin Z and branched Fomblin Y) are shown in Figure 5. In the same figure two lines with slopes of $-1/3$ and 1, respectively, are drawn to compare the experimental behavior with the predicted scaling behavior. The behavior of the linear polymer (Z) (a decreasing shear stress vs the shear rate) is in good qualitative agreement with regime 2. The behavior of the polymer (Y) can be accounted for by the theoretical regime 1 (where the stress increases with shear rate according to the linear law). For the same shear velocity these polymers may fall in different regimes because they have different segmental surface and bulk friction parameters. It is not unreasonable to assume that the (Y) polymer has a smaller surface friction, ζ_1, and therefore, the reduced velocity u/u_1 might be smaller for polymer Y simply because u_1 is larger.

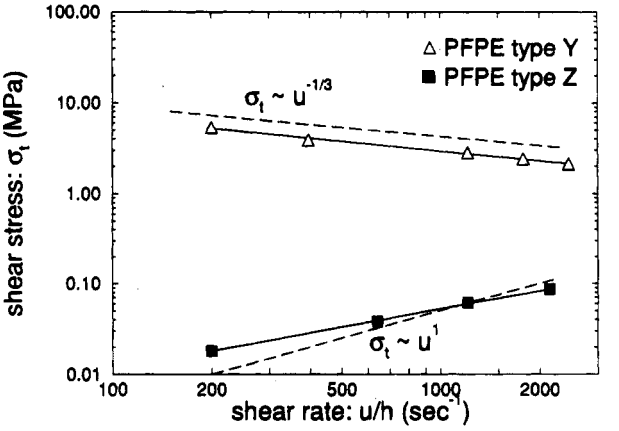

Figure 5. Shear stress vs shear rate: comparison with experiments.[1]

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